

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08G 18/18</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/02525</b> <b>(43) International Publication Date:</b> 3 February 1994 (03.02.94)
<b>(21) International Application Number:</b> PCT/EP93/01845 <b>(22) International Filing Date:</b> 14 July 1993 (14.07.93)  <b>(30) Priority data:</b> 9215488.9                      21 July 1992 (21.07.92)                      GB  <b>(71) Applicant (for all designated States except US):</b> POLYOL INTERNATIONAL B.V. [NL/NL]; Aert van Nesstraat 45, NL-3012 CA Rotterdam (NL).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> CASATI, Francois, Marie [FR/FR]; Résidence Rousseau, Route des Alpes, F-01280 Prévessin-Moëns (FR).  <b>(72) Inventor:</b> RISTEMA VAN ECK, Reinold (deceased).		<b>(74) Agent:</b> SMART, Peter, John; W.H. Beck, Greener & Co., 7 Stone Buildings, Lincoln's Inn, London WC2A 3SZ (GB).  <b>(81) Designated States:</b> AU, BR, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ISOCYANATE MODIFIED AMINES AS CATALYSTS USEFUL FOR THE PREPARATION OF POLYURETHANE MATERIALS  <b>(57) Abstract</b>  An isocyanate modified amine catalyst is prepared by intimately mixing under reaction conditions a reactive tertiary amine, a polyol, and a organic isocyanate compound. This isocyanate modified amine catalyst is useful for the preparation of polyurethane materials such as foams, with densities ranging between 15 and 500 kg/m <sup>3</sup> , molded or free rise, flexible, semi-flexible or rigid, integral ski, or microcellular foams, elastomers or coatings.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LJ	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

ISOCYANATE MODIFIED AMINES AS CATALYSTS USEFUL FOR THE  
PREPARATION OF POLYURETHANE MATERIALS

5 The present invention relates to a method of  
producing polyurethane materials by employing as a  
catalyst or co-catalyst an isocyanate modified amine  
which is prepared by reacting a tertiary amine  
containing a reactive hydrogen, a polyisocyanate and a  
polyol. The present invention also relates to  
10 polyurethane materials produced by the above method.

Tertiary amines are widely used as catalysts  
for the production of polyurethane foams, elastomers and  
coatings because they act to accelerate both water-  
isocyanate and polyol-isocyanate reactions.  
15

It is well established that the structure of a  
tertiary amine has a considerable influence on its  
catalytic effect and on its usefulness (see,  
"Polyurethanes, Chemistry and Technology", Interscience  
20 Publishers, by J.H. Saunders and K.C. Frisch, Part I,  
p.228 to 230).

Parameters to consider in selecting a tertiary  
amine catalyst are : basicity, steric hindrance of the  
amine nitrogen(s), volatility, hydrophylicity and  
25

solubility in the other raw materials used for the production of polyurethane materials.

5 Use of tertiary amines which do not contain active hydrogen sites (non-reactive tertiary amines) is often associated with problems of odor, toxicity, and staining of polyvinyl chloride (PVC) material molded against polyurethane foam. These tertiary amines have a strong odor which is carried over to the final polyurethane material. Potential inhalation toxicity of  
10 tertiary amines is also well known.

Tertiary amines containing active hydrogen sites (reactive tertiary amines) were thought to offer solution to the problems of odor, toxicity, and staining  
15 of the PVC material associated with non-reactive tertiary amines.

It was believed that reactive tertiary amines totally react with the isocyanate component and become part of the polyurethane backbone. This, it was  
20 believed, could provide reduced staining of the PVC material, while minimizing the odor and possible health hazards associated with free amine. However, numerous studies of the activity of reactive amine catalysts have  
25 shown that this is not always the case.

It has been found that amine catalysts containing hydroxyl groups and/or secondary or primary amines, are generally less active than the corresponding alkyl substituted derivatives. Furthermore, studies of  
30 reactive amine catalysts containing hydroxyl groups have shown that amines with primary hydroxyl groups are more effective catalysts than those with secondary hydroxyl

groups and those in turn are more effective than the analogous catalysts with tertiary hydroxyl groups.

5 It has also been shown that amine catalysts containing a primary or secondary amine group are not effective in reducing staining of PVC. This is surprising because reactive amine catalysts were expected to react with the isocyanate component and become part of the polyurethane backbone. Thus, it appears that reactive amine catalysts are not totally  
10 bound to the polyurethane backbone during the isocyanate-water and isocyanate-polyol reactions but rather form, in the same way as their corresponding alkyl derivatives, complexes with isocyanates and water, and are released when polyurethane reactions proceed.  
15 These reactive amines then can react with isocyanate and become tied up chemically to the polyurethane backbone, but only if there are free isocyanates left, which is not always the case.

20 Furthermore, part of reactive amine catalysts, especially when they are volatile, may be vaporized by the heat of the polyurethane reaction and may not be able to react with the isocyanate during the foaming stage. After cooling and condensation of the amine  
25 catalyst, there may be no free isocyanate left to react with it. All of this is confirmed by the findings of A.R. Nutt and D.W. Skidmore (Cellular Polymers, Vol. 6, 1987, p. 62) who detected DMEA (dimethyl amino ethanol) in scrubbers above a foaming plant using this amine as  
30 catalyst in the foam formulations.

Mechanism of action of tertiary amines and their performance in the production of polyurethane composition has been widely investigated and described in many publications such as, for example, the following.

publications: (1) "Choosing urethane foam catalysts" by Thomas E. Rusch et al., published in "Plastics Compounding", July-August 1980; (2) "Amine catalysts of Polyurethane foams", by N. Malwitz et al., in "Journal of Cellular Plastics" volume 23, September 1987; (3) 5 "Amine catalysis of the Aryl isocyanate reaction" by N. Malwitz and J.E. Kresta in "SPI-Polyurethane World Congress 1987", September 29-October 2, 1987, Aachen; (4) "Factors Affecting the Discoloration of Vinyl That 10 Has Been Molded Against Urethane Foam" by Robert L. Zimmerman and T.H. Austin, in "SPI-Polyurethane World Congress 1987", September 29-October 2, 1987, Aachen; (5) "Low odor reactive amine catalysts for Polyurethane foams" by R.L. Zimmerman and T.L. Renken, in SPI, 31st 15 Annual Technical Marketing Conference, October, 18-21, 1988, Philadelphia; (6) "New Amine Catalysts Providing Less Discoloration to PVC Covered Semi-Rigids Urethane Foam Products" by S. Arai et al., in 30th Annual 20 Polyurethane Technical/Marketing Conference, October 15-17, 1986, Toronto; (7) "Unusual Catalysts for Flexible Urethane Foams" by I.S. Bechara and F.P. Carroll, Proceedings of the SPI 24th Annual Urethane Division Technical Conference, Atlanta, Georgia, October 25 - 27, 25 1978; and (8) "Problems of Interaction Between Plasticized PVC and Polyurethane Foam" by A.S. Wilson, et al., Plastics and Rubber International, Vol. 13 No. 1, February 1988.

30 Isocyanate modified reactive amines are described in the literature.

US Patent 3,325,421 (E. Muller); US Patent 4,089,835 (K. König et al) and US Patent 4,093,569 (A. Reischl et al) disclose isocyanate modified amines and their use for producing stable dispersions of polyurea

in polyols. US Patent 4,089,835 also mentions the potential use of monofunctional amines or alkanolamines but only as chain terminators.

5 This is also the case in British Patent 2,072,204 which discloses formation of polymer modified polyol by polymerizing an olamine with an organic polyisocyanate in the presence of a polyol.

10 US Patent 4,041,019 and US Patent 4,007,140 describe polyurethane catalysts obtained by a modification of an amine with an isocyanate. The modified amines are 2-methylimidazole and 3-dimethyl-amino propylamine, respectively. However, no polyol is present and therefore no linkage with a high molecular weight chain is disclosed or hinted.

15 US Patent 5,034,426 (J. Casey et.al) discloses a catalytic chain extender comprising an aromatic diamine having a tertiary amine functionality incorporated into a side chain of the aromatic diamine and a process for the preparation of a polyurethane composition using this catalytic chain extender.

20 US Patent 4,456,696 and US Patent 4,517,313 disclose reactive amines modified by neutralization with acids.

European Patent 0,376,602 describes the alkoxylation of triamines and their use as polyurethane catalysts.

30 US Patent 4,040,992 discloses reactive amines modified by quaternarization.

However, there is no mention or hint in the literature of the use of isocyanate modified reactive amines as catalysts or co-catalyst in the production of polyurethane materials. Considering all aspects of polyurethane catalysis a skilled person would expect

that pre-reacting a tertiary amine containing a reactive group with a polyisocyanate and a polyol and using this modified amine to catalyze a polyurethane reaction would lead to a drastic drop in the performance of this modified reactive amine in comparison with the  
5 corresponding non-modified reactive amine, since the basis of the catalytic activity of an amine is its complexation with both the hydroxyl component and the isocyanate.

10 It has now surprisingly been found that this is not the case and that isocyanate modified amines produced by reacting a tertiary amine containing a reactive hydrogen, a polyisocyanate and a polyol show comparable or enhanced catalytic activity compared with  
15 the corresponding non-modified amines.

Accordingly, the present invention concerns an isocyanate modified amine catalyst prepared by intimately mixing under reaction conditions a reactive  
20 tertiary amine, a polyol, and an organic isocyanate compound.

In another embodiment, the present invention concerns a process for the preparation of a polyurethane material which comprises intimately mixing under  
25 reaction conditions a polyol, an organic isocyanate compound, at least one catalyst for the urethane forming reaction and, optionally, a blowing agent and/or one or more additives wherein said at least one urethane  
30 forming catalyst comprises an isocyanate modified reactive amine prepared by the aforementioned process.

Still in another embodiment, the present invention concerns a polyurethane material prepared by aforementioned process.



The isocyanate modified amine useful as a catalyst or co-catalyst in the process of the present invention is prepared by blending, in a suitable reaction vessel, a polyol and a reactive amine for a period of time from about several seconds to about several minutes, preferably from about 10 seconds to about 1 minute, most preferably from about 20 seconds to about 30 seconds, while stirring the blend. Then, while stirring the blend, a polyisocyanate is slowly added to the blend and the resulting reaction mixture is stirred for additional period of time of from about several seconds to about several minutes, preferably from about 10 seconds to about 1 minute, most preferably from about 20 seconds to about 30 seconds. The stirring is then discontinued while an exotherm reaction is completed. The resultant isocyanate modified amine can be a liquid of various viscosity or a gel. If this blending is made with a mixing head, these times can be reduced to a couple of seconds.

Any amine containing both tertiary nitrogen(s) and active hydrogen(s) can be employed in the present invention as the reactive amine. Preferably these amines contain at least one dialkyl, preferably dimethyl, amino group or one amidine function.

The chain between the active hydrogen and the nitrogen(s) can be of any length, preferably between 2 and 5 carbons with or without ether functions between them.

The active hydrogen is derived from an -OH group, a -NH group, or any chemical structure listed by Saunders and Frisch in "Polyurethanes", Part I, pages 65 to 88. Preferably, the active hydrogen is derived from an -OH or a -NH group.

Illustrative of suitable amines containing a reactive hydrogen are, for example, N,N-dimethylamino ethanol; N,N-dimethylamino propanol; N,N,N'-trimethyl-N'-(2-hydroxyethyl)ethylene diamine; 2-methyl-8-(3-hydroxypropyl)-2,8-diaza-5-oxanonane; N,N,N'-trimethyl-N'-(hydroxypropyl)ethylene diamine; 2-methyl-8-(2-hydroxypropyl)ethylene diamine; 2-methyl-8-(2-hydroxyethyl)-2,8-diaza-5-oxanonane; N,N,N'-trimethyl-N'-(ethoxyethanol)-ethylene diamine; 2-(N,N-dimethylamino)ethoxyethanol; 1,5,7-triazabicyclo-(4,4,0)-dec-5-ene; N,N-dimethylaminopropyl amine; piperazine; N-methyl-N'-(2-hydroxyethyl)-piperazine; 2,4,6-tris(dimethylaminoethyl) phenol; Bis(dimethylamino)propyl amine; 1,1,3,3-tetramethyl guanidine and compounds described in US Patent 4,957,944, and the like.

The isocyanates which can be used in the preparation of the modified amine useful in the present invention are polyfunctional isocyanates well known to those skilled in the art. Suitable polyisocyanates include aliphatic, cycloaliphatic and aromatic polyfunctional, particularly bifunctional, isocyanates. These include: aliphatic diisocyanates having between 2 and 18 carbon atoms, preferably between 4 and 12 carbon atoms, such as ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexa-methylene diisocyanate and 1,12-dodecane diisocyanate; cycloaliphatic diisocyanates having between 2 and 18 carbon atoms, preferably between 4 and 12 carbon atoms, such as cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate as well as any desired mixture thereof, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; 2,4- and 2,6-hexahydrotoluene diisocyanate as well as any desired mixture of these isomers; 4,4'- and 2,4'-diisocyanatodicyclo-

hexylmethane; aromatic diisocyanates such as 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate (TDI) as well as any desired mixture of these isomers, 2,2'-, 2,4'- and 4,4'-diphenylmethane diisocyanate (MDI) as well as any desired mixture of these isomers, oligomers of MDI (polymeric MDI), mixtures of TDI and polymeric MDI, and naphthylene-1,5-diisocyanate; aromatic polyisocyanates such as 4,4',4''-triphenylmethane triisocyanate, 2,4,6-triisocyanatobenzene and polyphenylene polymethylene polyisocyanates. Prepolymers of polyfunctional isocyanates and polyfunctional alcohols or amines can also be used.

Suitably, the reactive amine and the isocyanate are employed in a molar ratio of 0.1 to 10.

Polyols which are suitable for use in the preparation of the modified amine useful in the present invention are polyether polyols and polyester polyols. These polyols are well known and are readily available. Polyether polyols are preferred. The term polyether polyol includes alkylene oxide adducts of low molecular weight diols or triols of naturally occurring polyols and non-reducing sugars and derivatives thereof, having molecular weight between 500 and 15,000, preferably 1,000 to 6,000. Suitable polyether polyols can be prepared by adding an alkylene oxide to an initiator containing at least one and preferably two or more active hydrogen atoms.

Illustrative of commercially available polyether polyols suitable for use in the present invention include those products sold by The Dow Chemical Company under the trademarks VORANOL and VORALUX such as, for example, VORANOL CP-6001, VORANOL CP-3322, VORANOL CP-4702, VORALUX HF-500, and the like.

Other suitable polyols for use in the present invention include PHD -, PIPA - or SAN - type copolymer polyols. These polyols known as polymer polyols are commercially available. Illustrative of commercially available SAN - type copolymer polyols suitable for use in the present invention include those products sold by The Dow Chemical Company under the trademark SPECFLEX such as, for example, SPECFLEX NM 800.

Mixtures of one or more polyether polyols and/or one or more polymer polyols are also suitable for use in the present invention.

The isocyanate modified amines prepared as described hereinabove have good heat stability and once incorporated in the polyurethane matrix do not migrate with time or under high temperature conditions.

The process of the present invention provides the following advantages: (a) all amine odors in both the formulated raw materials and in the finished polyurethane product are considerably reduced or eliminated, (b) fogging due to volatile catalyst(s) in applications such as car seats or door panels is eliminated, (c) staining of PVC or of textile in applications such as dashboards, car seats, head rests etc, is drastically reduced, and (d) physical properties of polyurethane materials such as compression sets which can be affected by residual unreacted amine catalyst(s) are improved.

In making a polyurethane material according to the process of the present invention, the polyol(s), polyisocyanate, the hereinbefore described modified amine catalyst and, optionally, foaming agent and/or other components are contacted, thoroughly mixed and

permitted to react and to expand and cure into a polyurethane material. The particular mixing apparatus is not critical, and various types of mixing head and spray apparatus are conveniently used. It is often convenient, but not necessary, to preblend certain of the raw materials prior to reacting the polyisocyanate and polyol components. For example, it is often useful to blend the polyol(s), a suitable foaming agent, catalyst(s) and other components except for polyisocyanate(s), and then contact this mixture with the polyisocyanate. Alternatively, all components can be introduced individually to the mixing zone where the polyisocyanate(s) and polyol(s) are contacted. It is also possible to prereact all or a portion of the polyol(s) with the polyisocyanate(s) to form a prepolymer.

Suitable polyols and/or polymer polyols which can be used to produce the polyurethane materials of the present invention are well known in the art and include those hereinbefore described and any other commercially available polyol and/or polymer polyol. Mixtures of one or more polyols and/or one or more polymer polyols may also be used to produce the polyurethane materials according to the present invention.

In the process of the present invention, the hereinbefore described modified reactive amine catalyst can be used alone or in combination with known urethane catalysts. Exemplary of known catalysts which can be used in combination with the modified reactive amines of the present invention are amines, reactive or non-reactive, with aminated crosslinkers such as for instance urea, triethanolamine, and methyl

diethanolamine or organometallic compounds such as tin, bismuth, or zinc compounds and the like.

5       The levels of urethane catalysts used are conventional, but typically, depending on the specific catalyst, will be present in an amount of from 0.001 to 10.0, preferably from 0.01 to 5.0, most preferably 0.05 to 3.0 parts by weight.

10       Foaming agents which can be used to prepare polyurethane materials according to the present invention are well known in the art and include water and physical foaming agents. Exemplary of physical foaming agents which may be used include, for example, the halogenated hydrocarbons such as methylene chloride, 15 trichlorofluoromethane, dichlorotrifluoroethane, chlorodifluoroethane; hydrocarbons such as pentane and hexane; and entrained gases such as air, nitrogen and carbon dioxide.

20       The foaming agent when used may be present in an amount to provide the resulting polyurethane foam with an overall density of from 15 to 500 kg/m<sup>3</sup>.

25       Other conventional components which optionally, but advantageously are employed in the preparation of polyurethane foams, include surfactants such as, for example, Silicone Union Carbide SH-209 product sold by Union Carbide Corporation; chain 30 extending agents such as, for example, ethylene glycol, 1,4-butanediol, diethanolamine, diisopropanolamine and polyamine; fillers; fire-retardants, for example, melamine; pigments and dyes; and the like.

      The polyurethane materials prepared according to the present invention can be foams, with densities

ranging between 15 and 500 kg/m<sup>3</sup>, molded or free rise, flexible, semi-flexible or rigid, integral skin, or microcellular foams, elastomers or coatings.

The following terms and abbreviations are used in the examples bellow:

DEOA is diethanolamine.

BDMPA is bis(dimethylaminopropyl) amine.

TMHED is N, N, N'-trimethyl-N'-(2-hydroxyethyl) ethylene diamine.

DMAEE is 2-(dimethylaminoethoxy)ethanol.

MHEDON is 2-methyl-8-(2-hydroxyethyl)-2,8-diaza-5-oxanonane.

TDI is toluene diisocyanate.

TDI 80/20 is a mixture of 2,4- and 2,6- TDI in 80% - 20% ratio.

MDI is diphenylmethane diisocyanate.

PMDI is polymeric MDI.

M-309 is liquid MDI derivative having functionality of 2.2 and an isocyanate content of 32.3% sold by The Dow Chemical Company under the trademark ISONATE M-309.

M-220 is polymeric MDI having an average functionality of 2.7 and isocyanate content of 30.9% sold by The Dow Chemical Company under the trademark VORANATE M-220.

VM-50 is a blend of polymeric MDIs sold by Imperial Chemical Industries under the trademark SUPRASEC VM-50.

CP-3322 is a polyol having OH number of 48 and Average Molecular Weight of 3500 sold by The Dow Chemical Company under the trademark VORANOL CP-3332.

5 CP-1421 is a polyol having OH number of 33 and Average Molecular Weight of 5000 sold by The Dow Chemical Company under the trademark VORANOL CP-1421.

10 CP-4702 is a polyol having OH number of 35 and Average Molecular Weight of 4800 sold by The Dow Chemical Company under the trademark VORANOL CP-4702.

CP-6001 is a polyol having OH number of 27 and Average Molecular Weight of 6200 sold by The Dow Chemical Company under the trademark VORANOL CP-6001.

15 HF-500 is a polyol having OH number of 35 and Average Molecular Weight of 4800 sold by The Dow Chemical Company under the trademark VORALUX HF 500.

CA-560-1 is a polyol sold by Shell Chemicals under the trademark CARADOL 560-1.

20 NM-800 is a SAN copolymer polyol sold by The Dow Chemical Company under the trademark SPECFLEX NM-800.

25 NC-604 is a SAN copolymer polyol sold by The Dow Chemical Company under the trademark SPECFLEX NC-604.

30 33LV is a 33 percent solution of triethylene diamine in dipropylene glycol sold by Air Products and Chemicals Inc. under the trademark DABCO 33LV.

A-1 is 70% bis(2-dimethylaminoethyl)ether solution in DPG, an amine catalyst, sold by Union Carbide Corporation under the trademark NIAX A-1.



SH-210 and SH-209 are silicone surfactants sold by Union Carbide Corporation under the trademark Union Carbide SH-210 and Union Carbide SH-209 silicones.

5 DA-660 is a mold release agent sold by Grace Teroson under the trademark DARALESE 660.

LK-260 is a mold release agent sold by Th. Goldschmidt.

CT is cream time in seconds.

10 GT is gel time in seconds.

RT is rise time in seconds.

Wet CS is wet compression set at 70% CD with skin determined according to Renault test RP-16.37-81.

15 HACS is humid aged compression set at 75% CT determined according to ISO, BS 4443,79.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

20

25

30

EXAMPLE 1

## A. PREPARATION OF MODIFIED AMINE CATALYST

5 In a 250 ml glass bottle equipped with a magnetic stirrer CP-3322 (100 grams) and BDMPA (50 grams) were blended together for 30 seconds with stirring. Then, without stopping the stirring, TDI 80/20 (23.2 grams) was added slowly for 7 seconds to the  
10 blend and stirring was continued for another 30 seconds. Temperature rose to 66° C after 1 minute and then decreased to 35° C after 12 minutes. The resulting catalyst is designated as Catalyst A.

## 15 B. PREPARATION OF HR POLYURETHANE FOAM

High resilience polyurethane foam was prepared by employing the following procedure:

The components as indicated in Table 1 below were mixed intimately using a mixer running at a speed of  
20 about 2500 RPM and poured in a cardboard box for free-rise reactivity tests. Then the same blends based on 350 grams polyol for formulations A and C were placed in a 9 liter square aluminium mold kept at 55°C. LK 260  
25 was used as a mold release agent and the demold time was 7 minutes.

Foam formulations and properties of the foams obtained using Catalyst A and BDMPA are given in Table 1  
30 below.

Table 1

	<u>Formulations</u>	<u>A*</u>	<u>B</u>	<u>C</u>
	Polyol Blend (php) (CP-6001 and Copolymer Polyol (ACN/ST 50/50) 16% total solids	100	100	100
5	CP-14.21 (php)	2.0	2.0	2.0
	water (php)	2.8	2.8	2.8
	CATALYST A (php)		1.7**	2.0
	BDMPA (php)	0.5**		
10	SH-210 (php)	1.0	1.0	1.0
	Glycerol (php)	0.5	0.5	0.5
	Isocyanate Blend (80% TDI 80/20 and 20% PMDI) Index 100	35.4	35.2	35.2
15	<u>Free-Rise Reactivity</u>			
	cream time (s)	11	11	10
	gel time (s)	120	115	100
	rise time (s)	196	183	162
20	settle (mm)	20	15	20
	<u>Properties</u>			
	molded foam density (kg/m <sup>3</sup> )	49.9	NA	49.7
25	* not an Example of the present invention			
	** 1.7 php of Catalyst A is equivalent to 0.5 BDMPA			

EXAMPLE 2

## 30 PREPARATION OF MODIFIED AMINE CATALYSTS

Following the procedure described in Example 1A hereinbefore but using instead CP-3322 (10 grams) and the reactants and amounts set forth in Table 2 below, various modified amine catalysts were prepared. The

data and maximum exotherm temperatures measured are given in Table 2 below.

Table 2

	<u>AMINE</u>	<u>AMINE</u> <u>mmole</u>	<u>TDI</u> <u>80/20</u> <u>mmole</u>	<u>TEMP.</u> <u>°C</u>	<u>CATALYST</u>	<u>PHYS.</u> <u>STATE</u>
5	BDMPA	26,7	6,7	45	AA	liquid
	BDMPA	26,7	13,3	62	AB	liquid
	BDMPA	26,7	18,9	80	AC	visc. liquid
10	BDMPA	26,7	25,3	84	AD	gel
	TMHED	34,0	8,5	42	BA	liquid
	TMHED	34,0	16,0	62	BB	liquid
	TMHED	34,0	22,5	75	BC	gel
15	DMAEE	37,5	9,4	43	CA	liquid
	DMAEE	37,5	18,8	67	CB	liquid
	DMAEE	37,5	37,5	85	CC	gel
	MHEDON	26,3	6,6	38	DA	liquid
20	MHEDON	26,3	13,2	61	DB	liquid
	MHEDON	26,3	19,5	71	DC	gel

The prepared modified amine catalysts were left at room temperature for several days before using them in the preparation of polyurethane foams.

EXAMPLE 3

30 PREPARATION OF MODIFIED AMINE CATALYSTS

Following the procedure described in Example 1A hereinbefore but using instead CP-3322 (100 grams) and the reactants and amounts set forth in Table 3 below, two modified amine catalysts were prepared. The data

and maximum exotherm temperatures measured are given in Table 3 below.

Table 3

5	<u>AMINE</u>	<u>AMINE</u> <u>mmole</u>	<u>TDI 80/20</u> <u>mmole</u>	<u>TEMP.</u> <u>°C</u>	<u>CATALYST</u>	<u>PHYS.</u> <u>STATE</u>
	BDMPA	53	53	55	AE	liquid
	MHEDON	53	53	46	DD	liquid

10       The prepared modified amine catalysts were left at room temperature for several days before using them in the preparation of polyurethane foams.

EXAMPLE 4

15   PREPARATION OF POLYURETHANE FOAMS

Following the procedure described in Example 1B hereinbefore but using instead the foam formulation set forth in Table 4 below various polyurethane foams were  
20   prepared.

Table 4

	<u>Foam Formulation</u>	<u>php</u>
	CP-4702	50.0
25	NM-800	50.0
	CA-560-1	5.0
	water	2.0
	Catalyst	see Table 5
30	VM-50       Index 102	46

Catalysts used in the above foam formulation and physical properties of the obtained polyurethane foams are set forth in Table 5 below.

Table 5

	<u>CATALYST</u>	<u>CATALYST</u> <u>(php)</u>	<u>CT (s)</u>	<u>GT (s)</u>	<u>RT (s)</u>	<u>FOAM</u> <u>DENSITY</u> <u>kg/m<sup>3</sup></u>
5	BDMPA*	0.90	19	94	145	91.0
	AA	2.91	20	100	163	93.1
	AB	3.12	20	101	166	92.7
	AE	10.74	20	105	168	95.0
10	TMHED*	0.60	21	99	164	84.7
	BA	1.98	21	106	177	86.8
	BB	2.14	22	110	185	86.1
	DMAEE*	0.8	18	93	149	85.0
	CA	2.66	20	103	167	88.7
15	CB	2.92	22	105	169	86.5
	MHEDON*	0.30	15	130	203	82.3
	DA	1.0	15	129	192	81.6
	DB	1.05	18	138	210	81.0
20	DD	3.70	18	140	210	83.2

\* not an Example of the present invention

EXAMPLE 5

25 PREPARATION OF MODIFIED AMINE CATALYSTS

Following the procedure described in Example 1A  
 hereinbefore but using instead CP-3322 (10 grams) and  
 the reactants and amounts set forth in Table 6 below,  
 30 various modified amine catalysts were prepared. The  
 data and maximum exotherm temperatures measured are  
 given in Table 6 below.

Table 6

	<u>AMINE</u>	<u>AMINE</u> <u>grams</u>	<u>M-309</u> <u>grams</u>	<u>TEMP.</u> <u>°C</u>	<u>CATALYST</u>	<u>PHYS.</u> <u>STATE</u>
	MHEDON	5	3.4	59	DE	liquid
5	MHEDON	5	5.1	67	DF	visc. liquid
	BDMPA	5	3.5	65	AF	liquid
	BDMPA	5	5.2	82	AG	gel
	TMHED	5	4.4	66	BD	liquid
10	TMHED	5	5.8	76	BE	visc. liquid
	TMHED	5	8.8	102	BF	gel

15

EXAMPLE 6

CP-3322 (10 grams) and TDI 80/20 (2.3 grams) were mixed together with stirring for 30 seconds and then BDMPA (2.5 grams) was added while stirring was continued. The resulting solution became quickly viscous and a gel was formed after cooling.

20

EXAMPLE 7

A solution of 9.1% BDMPA in CP-3322 (Solution A) was prepared.

A sample of each of Solution A above and Catalyst AE prepared in Example 3 were subjected to head-space chromatography using the following test conditions: a 15 ml penicillin flask hermetically closed with a septum and containing 1 gram of the sample was heated in a thermostatic bath at 100° C for 20 minutes before injection of its vapor phase into the RTX 35 gas chromatography capillary column (sold by RESTEK Corporation). The column was 30 meters in length and

30

0.32 mm in diameter. Detection was made by flame ionisation (fid) at 300° C, the gas carrier was helium at an output of 1 cm<sup>3</sup>/min. Temperature program was 5 minutes at 60° C, then the temperature was increased at a rate of 15° C/min. until 280° C, and then 10 min. at 280° C. The results are as follows:

Solution A\* Peak of BDMPA at 18.33 minutes retention time and area 96.8%

Catalyst AE no peak of BDMPA

\* not an Example of the present invention.

A sample of unaged Catalyst AE was also subjected to infrared spectroscopy to determine the existence of free isocyanate groups. No presence of any free isocyanate group was detected in unaged Catalyst AE by infrared spectroscopy.

#### EXAMPLE 8

##### A. PREPARATION OF MODIFIED AMINE CATALYSTS

Following the procedure described in Example 1A hereinbefore, but using the reactants and amounts set forth in Table 7 below, the following three modified amine catalysts were prepared.

Table 7

<u>AMINE</u>	<u>AMINE (grams)</u>	<u>TDI 80/20 (grams)</u>	<u>CP-33.22 (grams)</u>	<u>CATALYST</u>
BDMPA	10	9.2	100	AI
TMHED	10	13.1	88	BG
MHEDON	10	10.0	67.2	DG



## B. PREPARATION OF HR MOLDED POLYURETHANE FOAMS

High resilience molded polyurethane foams were prepared according to the procedure described in Example 1B using the formulation given in Table 8 below. Demold time was 5 minutes.

Table 8

<u>Foam Formulation</u>		<u>php</u>
CP-47.02		18.0
CP-33.22		5.0
NC-604		77.0
SH-209		0.6
Water		2.8
Catalyst	see Table 9	
Isocyanate Blend		34.7
(80% TDI 80/20 and 20% PMDI) Index 100		

Amine Catalysts used in the above foam formulation and physical properties of the obtained polyurethane foams are set forth in Table 9 below.

Table 9

	<u>CATALYST</u>	CATALYST	CT/GT/RT (s)	MOLDED DENSITY (kg/m <sup>3</sup> )	HACS 75%	WET CS 70%
		LEVEL (php)			(s)	(s)
	A-1/33LV*	0.1/04	5/75/100	50.7	17.7	23.9
	A-1/33LV*	0.1/0.5	5/62/88	48.7	19.8	23.8
	A-1/33LV*	0.1/0.6	5/58/79	50.2	19.2	24.2
	TMHED/33LV*	0.1/0.5	6/75/100	51.4	17.7	22.1
	TMHED/33LV*	0.15/0.5	5/72/98	50.0	20.6	22.3

	CATALYST	CATALYST LEVEL (php)	CT/GT/RT (s)	MOLDED DENSITY (kg/m3)	HACS 75% (s)	WET CS 70% (s)
	BG/33LV	1.1/0.5	5/75/112	52.0	17.5	19.2
5	BG/33LV	1.67/0.5	5/70/105	51.3	16.9	21.6
	MHEDON/33LV*	0.1/0.5	5/65/105	50.8	18.8	23.4
	MHEDON/33LV*	0.15/0.5	4/50/85	49.9	21.9	24.6
	DG/33LV	0.87/0.5	5/67/97	50.6	16.3	19.3
	DG/33LV	1.31/0.5	4/62/88	50.0	19.3	22.3
10	BMPDA/33LV*	0.1/0.5	6/75/110	50.3	17.8	21.0
	BMPDA/33LV*	0.15/0.5	5/70/105	51.1	20.2	24.4
	AI/33LV	1.19/0.5	5/80/113	51.0	16.8	18.7
	AI/33LV	1.79/0.5	NA	50.9	16.4	17.3

15

\* not an Example of the present invention.

#### EXAMPLE 9

##### 20 A. PREPARATION OF MODIFIED AMINE CATALYSTS

HF-500 (90.68 grams) was blended with TMHED (5.84 grams) and then TDI 80/20 (3.48 grams) was added to the blend under stirring for 30 seconds. The resulting catalyst is designated as Catalyst E.

25

##### B. PREPARATION OF HR MOLDED POLYURETANE FOAMS

Semi-rigid molded polyurethane foam was prepared using Kraus Maffei machine model KM-40. The foam formulation and foaming conditions are given in Table 10 below. DA-660 was used as the mold release agent. Demold time was 5 minutes.

30

Table 10

	<u>Foam Formulation</u>	<u>php</u>
	Polyol Blend HF-500 and NM-800 (6% total solids)	100
5	Water	4.05
	DEOA, 88% in water	1.15
	Catalyst E	8.20
	M-220 (Index 100)	76.8
10	<u>Foaming Conditions:</u>	
	Polyol temperature	25° C
	Isocyanate temperature	25° C
	Recirculation pressure	180 bars
15	Total output	131.6 g/s
	Mold temperature	48° C
	Mold type	steel
20	Cream time (s)	6
	Gel time (s)	62
	Rise time (s)	120
	Free rise density	39.2 kg/m <sup>3</sup>
25	Molded density	120 kg/m <sup>3</sup>

30 A piece of molded foam produced using the above formulation was wrapped in a PVC foil which was then welded around it. This PVC wrapped foam is designated Foam A.

Similarly, a piece of foam produced using conventional reactive amine catalyst was also wrapped in a PVC foil which was then welded around it. This PVC wrapped foam is designated Foam B.

Ageing tests were run on both Foam A and Foam B in an oven for 500 hours at 80° C. Then using a Minolta Chromometer CR 200 and taking an unaged PVC sample as reference the change in color and lightness of the PVC sample, in contact with Foam A and Foam B was measured. Results are given in Table 11 below.

Table 11

	<u>PVC Sample</u>	<u>Foam A</u>	<u>Foam B*</u>
Lightness	L = 71.43	L = 71.50	L = 70.12
Red	a = + 2,05	a = + 2,31	a = + 3.48
Yellow	b = + 10,42	b = + 10,45	b = + 10,68
$\Delta E$		0.27	1.95

\* not an Example of the present invention

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

## WHAT IS CLAIMED IS:

1. An isocyanate modified amine catalyst  
5 prepared by intimately mixing under reaction conditions a reactive tertiary amine, a polyol, and an organic isocyanate compound.
2. An isocyanate modified amine of Claim 1  
10 prepared by first blending the reactive amine and the polyol under stirring for a period of time of from several seconds to several minutes, then slowly adding the organic isocyanate compound to the stirred blend,  
15 continuing to stir the resulting reaction mixture for a period of time of from several seconds to several minutes, then discontinuing the stirring and allowing the reaction mixture to exotherm.
3. An isocyanate modified amine of Claim 1 or  
20 Claim 2 wherein the reactive amine employed contains both tertiary nitrogen(s) and active hydrogen(s).
4. An isocyanate modified amine of any one of  
25 Claims 1 to 3 wherein the reactive amine employed contains an -OH or a -NH group.
5. An isocyanate modified amine of any one of  
Claims 1 to 4 wherein the reactive amine employed  
30 contains at least one dialkyl amino group or one amidine function.
6. An isocyanate modified amine of any one of  
Claims 1 to 5 wherein the organic isocyanate employed is a polyfunctional isocyanate or a prepolymer thereof and the polyol employed is a polyether polyol or polyester.

-28-

polyol having molecular weight between 500 and 15,000, a polymer polyol or any mixture thereof.

7. An isocyanate modified amine of any one of Claims 1 to 6 wherein the reactive amine and the  
5 polyfunctional isocyanate are employed in a molar ratio of 0.1 to 10.

8. A process for the preparation of a  
10 polyurethane material comprising intimately mixing under reaction conditions a polyol, an organic isocyanate compound, at least one catalyst for the urethane forming reaction and, optionally, a blowing agent and/or one or more additives wherein said at least one urethane  
15 forming catalyst is an isocyanate modified reactive amine catalyst of any one of Claims 1 to 7.

9. A process according to Claim 8 wherein a  
20 conventional urethane catalyst is employed as a co-catalyst.

10. A process according to Claim 8 or Claim 9  
wherein the polyol employed is a polyether polyol or polyester polyol having molecular weight between 500 and  
25 15,000, a polymer polyol or any mixture thereof and the organic isocyanate employed is a polyfunctional isocyanate or a prepolymer thereof.

11. A polyurethane which is the product of a  
30 polyurethane forming reaction in which polyurethane forming ingredients are reacted under the influence of a catalyst for the urethane forming reaction which is itself the product of reacting a reactive tertiary amine, a polyol, and an organic isocyanate compound.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01845

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08G18/18		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08G	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,2 080 960 (BAYER) 26 November 1971 see claim 1 see page 1, line 28 - line 32 see page 2, line 25 - line 29 see page 3, line 11 - line 32 see page 5, line 11 - line 17 ----	1-5,8
A	FR,A,2 085 965 (DOW) 31 December 1971 see claims 1-7 see page 3, line 9 - line 28 ----	1
A	DE,B,1 040 233 (HUDSON FOAM PLASTICS) 2 October 1958 see claim 1 see example 2 -----	1
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"d" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 OCTOBER 1993	22.10.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VAN PUymbROECK M. A.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9301845  
SA 77056

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/10/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2080960	26-11-71	DE-A- 2005115	19-08-71
		AT-A, B 306188	15-02-73
		BE-A- 762579	16-07-71
		GB-A- 1339730	05-12-73
		NL-A- 7101433	09-08-71
FR-A-2085965	31-12-71	BE-A- 765547	11-10-71
		DE-A- 2116535	09-12-71
		GB-A- 1338275	21-11-73
		NL-A- 7104678	12-10-71
DE-B-1040233		FR-A- 1139793	